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Lithium and magnesium perchlorate solutions and their influence on the rate and equilibrium of some cycloaddition reactions

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Abstract

Unusual high solubility of lithium perchlorate in diethyl ether (up to 6 M) allowed considering this solution as melted salt. Extensive investigations allow declaring that in salt solutions the rates and selectivity of all known chemical reactions have to differentiate from those in pure solvents. Large volume of data on lithium and magnesium perchlorates solubility, their effects on the chemo-and stereoselectivity, yield of product were accumulated at the present time and discussed in series reviews and monograph. Here the own and literature quantitative data on the heat of salt solution, partial molar volume, acceleration of reaction rate and equilibrium changes in the presence of common Fridel-Crafts catalysts, and lithium and magnesium perchlorates in some n-donor solvents, and the factors determining these affections on some (4+2)-, (3+2)-and (2+2)-cycloaddition reactions have been discussed. Several explanations of the acceleration effect of reactions in lithium and magnesium perchlorates solutions have been offered: (1) the increased internal pressure of salt solutions; (2) the possible catalysis by the Li+ and Mg2+ cations as a Lewis acid; (3) the drastic enhance of the polarity of salt solutions; and (4) the solvophobic interaction of the reagents, just as observed in going from common organic solvents to water or to saltingout salt solutions.